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Heat-resistant PMMA photonic crystal films with bright structural color

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ABSTRACT

Weak heat resistance of polymethylmethacrylate (PMMA) photonic crystal films has been the major challenge for its applications in displays or paints. This paper presents heat-resistant PMMA photonic crystal films with a bright structural color that are produced by using a simple preparation strategy. In this strategy, the heat resistance was controlled and remarkably improved by introducing methacrylic acid as comonomer together with methyl methacrylate. The mechanism of improving heat resistance was characterized by using scanning electron microscopy and differential scanning calorimetry. Three-dimensional ordered structures are produced, directly forming photonic crystal films that are highly heat-resistant and have a bright structural color. These two properties are significant for applications in displays or paints.

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1. Introduction

Photonic crystals are one class of functional materials with a periodicity in dielectric constant, which can control and manipulate light [1–7]. The ability of the crystals to control and manipulate light is important for their applications in full-color displays, paints, photonic paper, switches, modulators, and filters [8–10]. Among various technical applications, the direct conversion of light to color (structural color) has received significant attention because of its unique characteristics such as energy conservation. Considering their unique characteristics, artificial structural color films made through colloidal crystallization self-assembly, dielectric layer stacking, and direct lithographic patterning have received considerable attention in recent years [11]. In contrast to the expensive and non-scalable technologies of dielectric layer stacking and direct lithographic patterning, colloidal crystallization self-assembly is most frequently used in making photonic crystals because raw materials are easily obtained, and self-assembly is quite simple [11]. Among the materials used for producing photonic crystals through colloidal crystallization self-assembly, polymethylmethacrylate (PMMA), which is weather resistant, durable, and chemically stable, is of great significance [12–16]. Sotomayor Torres et al. successfully used PMMA beads to obtain photonic crystal structural color films by drying the spread latex; the film typically appears iridescent in the visible range [17]. Zhu et al. obtained P(NIPAm-*co*-MAA) hydrogel photonic crystal microparticles with inverse-opal structure by a combination of microfluidic and templating methods, which can respond to pH simultaneously due to the existence of MAA functional groups [18]. Chen et al. loaded $Cd_{0.4}Zn_{0.6}S$ nanocrystals on the surface of PS-*co*-PMAA microspheres. The obtained hybrids of integrating electronic confinement and photonic confinement, opened promising avenues in the design and construction of next-generation photoelectric devices based on photonic crystals [19]. Gu et al. prepared PMMA inverse opals, which could be stretched nearly 100% with diffraction peak blue-shifting across the whole visible spectrum [20]. However, the tuning color was not reversible because of the plastic deformation of the PMMA sheet [21]. Simultaneously, emulsion polymerization is a commonly used method of obtaining polymer microspheres from the free radical polymerization of vinyl monomers [22–24]. Copolymerization with functional monomers could achieve effective modification of polymer, which is of great significance to specific applications. Methacrylic acid (MAA) is typically used as comonomer to modify polymer such as polymethylmethacrylate (PMMA) and polystyrene (PSt). Robin et al. successfully encapsulated ZnO nanoparticles by P(MMA-MAA). MAA units of the obtained copolymer shell acted as a coupling agent, which then grafted onto polypropylene [25].

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Table 1
Effect of MAA concentration on particle size and size distribution of PMMA particles.

MAA (wt%)	Z-Ave (nm)[a]		PDI	Zp (mV)
	D_h	D_a		
0	286	254	0.02	−35.3
10.3	314	270	0.03	−34.3
18.7	348	301	0.05	−38.7
25.6	380	329	0.05	−40.3

[a] D_h: Hydrodynamic size of these microspheres measured by nanoparticle size measurement. D_a: Actual measured diameters from the SEM.

The persistence of photonic crystal structural color is crucial for its actual application in full-color displays, paints, and photonic paper. Once the periodic array is destroyed, the structural color will disappear. Therefore, the periodic arrays of photonic crystals should have high structural stability even under unstable environments. Among various external factors, temperature is very important because system temperature will increase as a result of the large thermal energy generated during solar radiation or laser irradiation [26–28]. However, PMMA has poor heat resistance because of its low glass transition temperature, which ranges from 40 °C to 100 °C [29–31], which severely limits the application of PMMA photonic crystal films.

In this report, heat-resistant photonic crystal structural color films were fabricated by assembling microspheres of methyl methacrylate (MMA) and methacrylic acid (MAA) through a vertical-lifting process. Three-dimensional ordered structures are achieved to form polymer crystal films that have a bright structural color. The introduction of MAA improves the heat resistance of photonic crystal films because copolymer has high spatial structure stability and temperature resistance [32]. Therefore, heat-resistant PMMA structural color films that have a bright structural color are obtained.

2. Experimental

2.1. Materials

MMA, MAA, and potassium peroxydisulfate (initiator) were purchased from Sinopharm Chemical Agent Company (Shanghai, China). All chemical reagents were used as received and without further purification.

2.2. Preparation of PMMA microspheres

The following were gradually added to a 250 ml three-necked flask: 150 ml deionized water, 8.7 g MMA, and a certain amount of MAA. After the mixture was heated to 80 °C in a water bath under a N_2 gas atmosphere, 0.080 g of initiator was added. Five hours later, the microsphere emulsion from the copolymerization of MAA and MMA was obtained.

2.3. Preparation and characterization of photonic crystal films

25 ml emulsion of PMMA spheres was poured into a 25 ml beaker, and then the beaker was placed in a Coater with Heatment (SYDC-100H DPI, SAN-YAN Instrument Co. Ltd., Shanghai). Glass slides were used as a substrate, and the pulling rate was set to 1 μm/s. The whole process was carried out at 25 °C. Glass slides were immersed in chromic acid lotion for 12 h and washed carefully before being used.

A Nanoparticle Size and Zeta Potential Measurement (Zetasizer Nano Series Nano-ZS90, Malvern, UK) were used to measure the hydrodynamic sizes and zeta potential of the particles. Optical photographs of the films were taken by using a Nikon digital camera. Scanning electron micrographs (SEM) were taken by using Nova NanoSEM 450 to observe the surface microstructures of the photonic crystal films. All the samples were coated with gold before

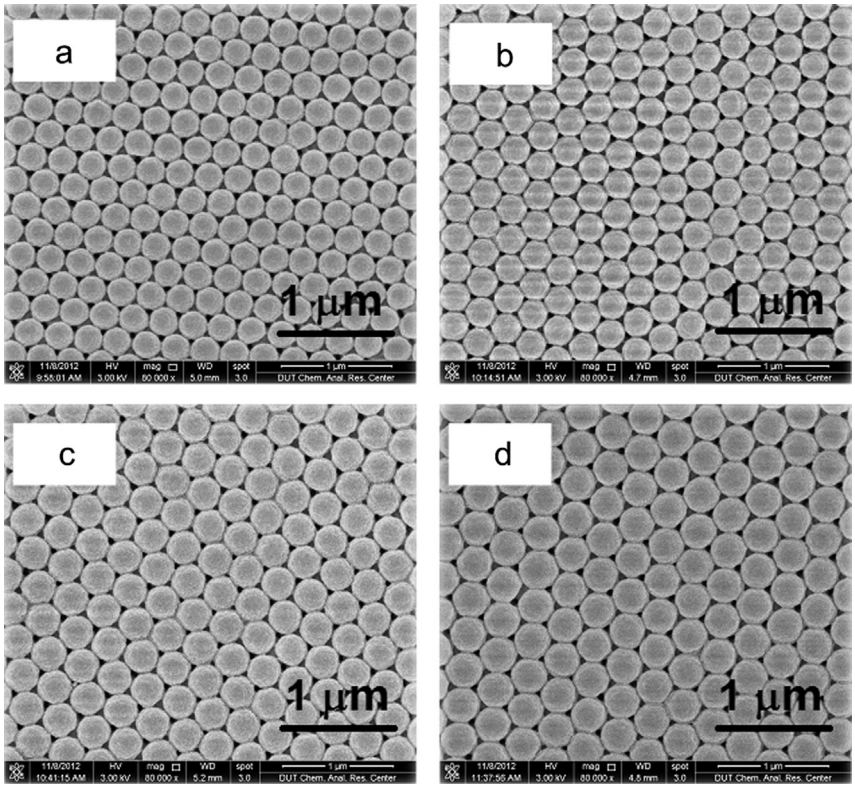

Fig. 1. SEM images of copolymer microspheres with varying MAA contents. (a) Pure PMMA, (b) 10.3 wt%, (c) 18.7 wt%, (d) 25.6 wt%.

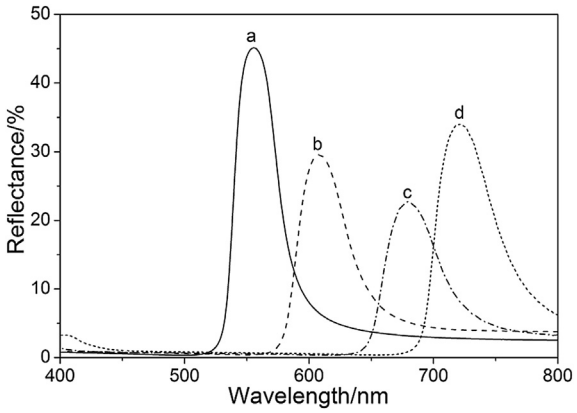

Fig. 2. Reflection spectra of films with varying MAA contents. (a) Pure PMMA, (b) 10.3 wt%, (c) 18.7 wt%, (d) 25.6 wt%.

observation. The reflection spectra of the films, which ranged from 400 nm to 800 nm, were measured by using a Hitachi U-4100 spectrophotometer. Differential scanning calorimetry (DSC) was performed in a nitrogen atmosphere by using an American TA Instruments 910S DSC thermal analyzer from −20 °C to 200 °C at a heating rate of 5 °C/min. FTIR spectroscopic analyses of the film samples were conducted in transmission mode by using a Thermo Scientific Nicolet 6700 FTIR spectrometer.

3. Results and discussion

PMMA microspheres were prepared through the method of emulsion copolymerization. Table 1 shows the effect of MAA content on particle size and size distribution of PMMA particles. Monodisperse particles that have MAA content that varies between 0 wt% and 25.6 wt% are obtained. The hydrodynamic size of these microspheres increases monotonically from 286 nm to 380 nm. The actual measured diameters from the SEM results are 254, 270, 301, and 329 nm, which are smaller than the hydrodynamic size. Polydispersity index (PDI) of the obtained microspheres ranges from 0.02 to 0.05, and the corresponding zeta potential ranges from −34.3 mV to −40.3 mV. PDI and zeta potential results indicate that a stable monodispersed emulsion is prepared [33].

After vertical-lifting assembly, the three-dimensional ordered structures were achieved. Fig. 1 shows the SEM images of the microstructure of photonic crystal films with varying MAA contents. The uniformly-sized beads are arranged in an orderly array. The size of the microspheres increases along with the increasing amount of MAA. The three-dimensional ordered structure can be further confirmed through the reflection spectra of polymer films in Fig. 2. All films with 0, 10.3, 18.7, and 25.6 wt% MAA show sharp reflectance peaks at wavelengths of 557, 608, 680, and 721 nm. On the macro vision, structural color changes from green to red, as indicated in Fig. 3. Bright structural colors are achieved because of an ordered structure (Fig. 1). Compared with pure PMMA film, films with MAA show lower reflectance. It possibly results from the increase of PDI. As shown in Table 1, PDI increased from 0.02 to 0.05 when MAA was added. The increased PDI indicates that size distribution of microspheres turns wider and consequently leads to the reduction of reflectance.

According to Bragg's law, the stop band and the color of a three-dimensional periodic structure can be explained by using the following equation:

$$\lambda = 2d\sqrt{n^2 - \sin^2\theta} \tag{1}$$

where n is the effective refractive index of materials; d is the distance between the crystalline planes in the (111) direction and is related to the polymer sphere diameter D by $d = \sqrt{2/3}D$ for the face-centered cubic (fcc) structure; and $\theta = 10^\circ$ is the angle of incident light. In addition, the effective refractive index n is determined by the filling ratio (f) of the microparticles as follows:

$$n = \sqrt{n_p^2 f + n_b^2(1-f)} \tag{2}$$

where $f = 0.74$ is the filling ratio for the polymer in the fcc structure. n_p and n_b denote the refractive index of the polymer and background materials, respectively. If the position of the stop band is within the visible range, the films display colors. The peak position of the stop band and the color of the crystal films depend on the relative filling ratio and the diameter of the polymer spheres. Here, $n_p = 1.48$ and $n_b = n_{air} = 1$, and the calculated peak positions of the stop bands for the photonic crystal films made of polymer spheres that are 254, 270, 301, and 329 nm in diameter are 563, 602, 671, and 716 nm, respectively. These values roughly match the experimental peak positions of 557, 608, 680, and 721 nm, as shown in Fig. 2.

The FTIR spectrum can provide valuable information about the structure of the materials, which means that it can clearly reveal the copolymerization of MMA and MAA. For an accurate reflection

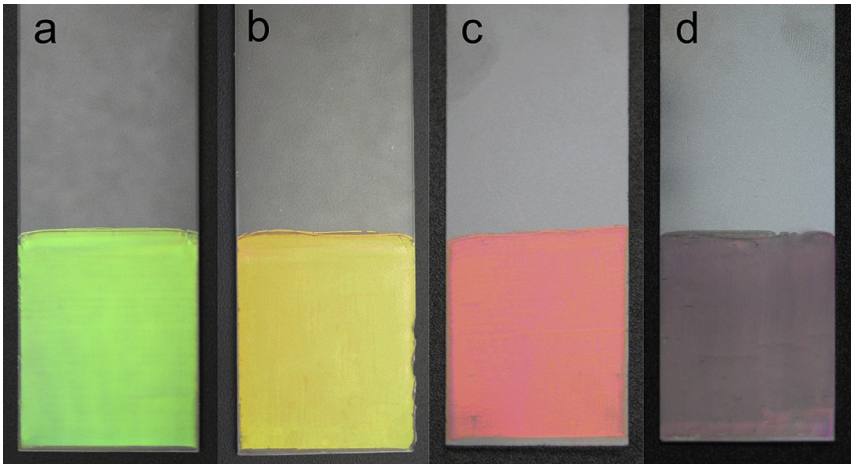

Fig. 3. Photographs of polymer films with varying MAA contents. (a) Pure PMMA, (b) 10.3 wt%, (c) 18.7 wt%, (d) 25.6 wt%.

of carboxy hydroxyl group in copolymers, we chose the paraffin paste method to avoid the interference of water contained in KBr. FTIR spectra for PMMA with varying MAA contents are shown in Fig. 4a. The one on the top of Fig. 4a is the curve of pure PMMA; it does not show the O–H bond at 3253 cm^{-1}. This peak becomes stronger with increased MAA (Fig. 4a). The broad peak at 2840 cm^{-1} to 2970 cm^{-1} is caused by the paraffin. However, carbonyl group stretching peaks of carboxylic acid and carboxylic ester overlap completely at 1730 cm^{-1}.

To distinguish between the carboxy carbonyl group and the ester carbonyl group, we used Na_2CO_3 as the basic reagent and tested the FTIR spectra after regulating the emulsion to pH 9. At this moment, carboxylic acid exists in the form of carboxylic salt. Fig. 4b shows the spectra, the one on the top is the curve of pure PMMA, and it displays only the C=O bond at 1722 cm^{-1}. However, the copolymer (Fig. 4b) also exhibits C=O stretches at 1566 cm^{-1}, which indicates the presence of carboxylic salt.

In summary, the O–H bond at 3253 cm^{-1} in Fig. 4a and the C=O bond at 1566 cm^{-1} in Fig. 4b proves the copolymerization of MMA with MAA.

Heat resistance is an important property for polymers. To date, all reported photonic crystal films of PMMA have poor heat resistance because of their low glass transition temperature (T_g). The DSC analysis (Fig. 5a) shows that the glass transition temperature of

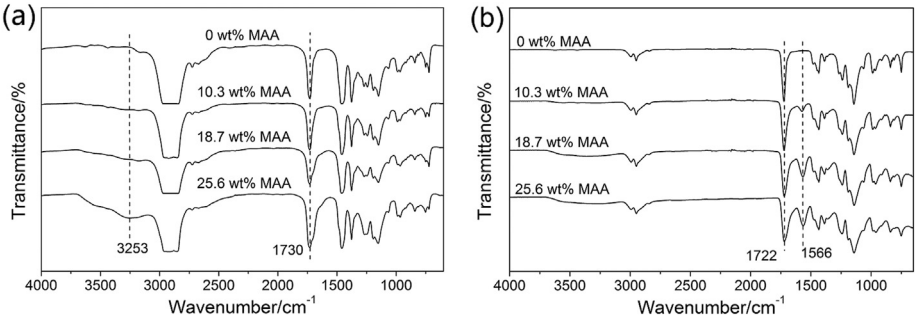

Fig. 4. FTIR spectra of PMMA with varying MAA contents. (a) Spectra used infrared paraffin paste method, (b) Spectra after regulating pH.

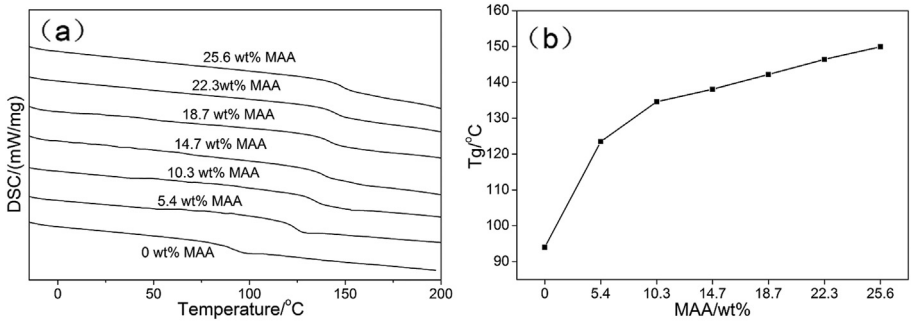

Fig. 5. DSC curves (a) and the corresponding T_g (b) of samples with varying MAA contents.

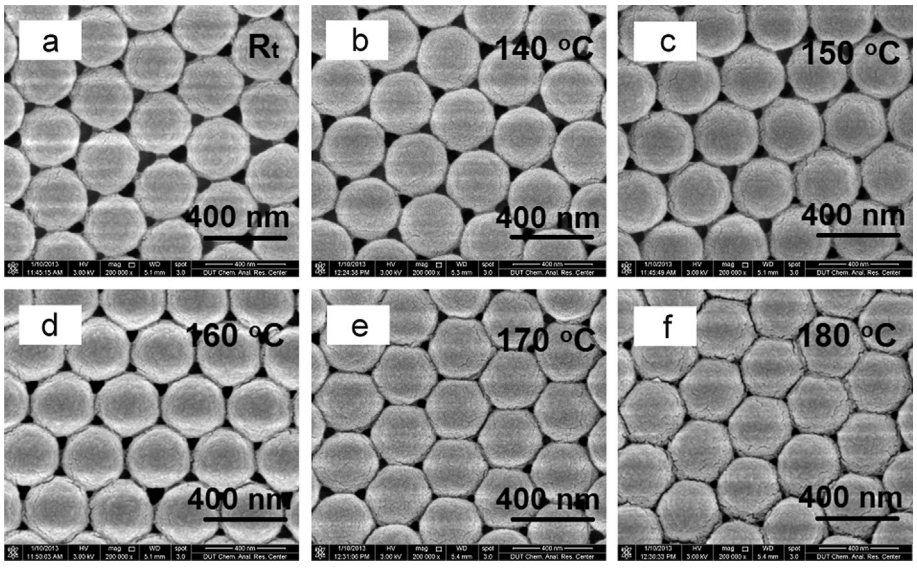

Fig. 6. SEM images of PMMA photonic crystal films with 18.7 wt% MAA under various temperature. Rt: Room temperature.

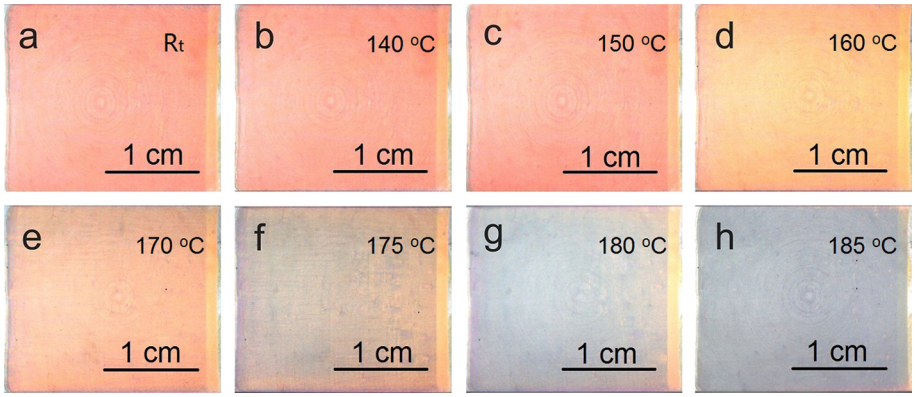

Fig. 7. Photographs of photonic crystal films with 18.7 wt% MAA under various temperature. Rt: Room temperature.

PMMA particles is improved when MAA is used. Pure PMMA has a heat flow change at 94.1 °C, which corresponds to the T_g of PMMA [34]. Nevertheless, the photonic crystal films with 18.7 wt% MAA shows a much higher T_g at about 145 °C (Fig. 5a), which is higher than that of pure PMMA by about 50 °C. The difference is ascribed to the confinement of intercalated PMMA chains [35] and demonstrates that the copolymer has better heat resistance than pure PMMA. As we can see in Fig. 5b, a small amount of MMA can increase the T_g of the polymer dramatically. Increasing the amount of MAA has little influence on T_g when the copolymer contains more than 18.7 wt% MAA.

Photonic crystal structural colors are closely related to their periodicity order [36]. Once the periodicity order is destroyed by heat, the structural color disappears. SEM was used to observe

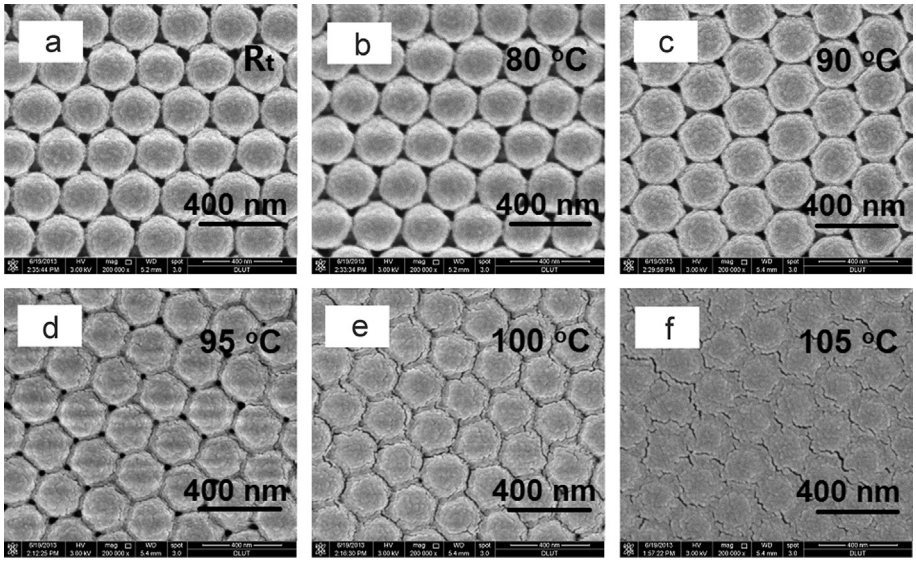

Fig. 8. SEM images of pure PMMA photonic crystal films under various temperature. Rt: Room temperature.

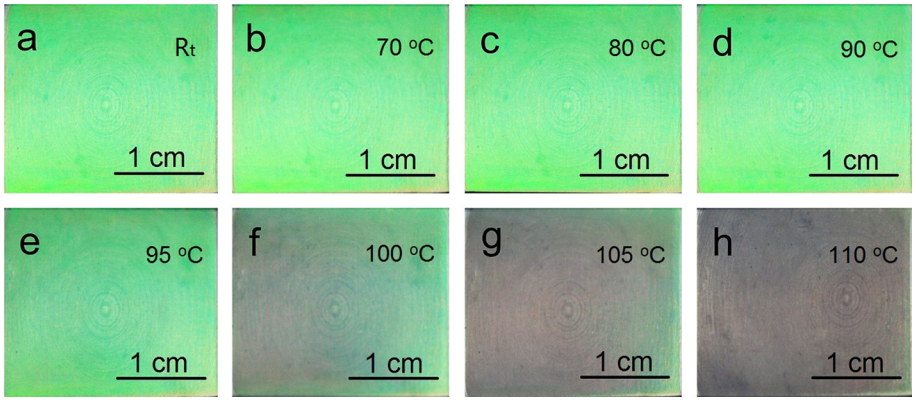

Fig. 9. Photographs of pure MMA photonic crystal films under various temperature. Rt: Room temperature.

surface microstructure changes in these photonic crystal films during heating. As shown in Fig. 6, the beads of PMMA photonic crystal films with 18.7 wt% MAA are arranged uniformly with voids. However, as a result of the increasing temperature, microspheres deform, and voids shrink gradually after exceeding the T_g of copolymers. The effective refractive index decreases at the same time. As a result, the structural color fades, as indicated in Fig. 7. When the temperature reaches 180 °C, the voids disappear, which then results in the disappearance of color. Pure PMMA films show similar properties, while the microspheres' deformation temperature is much lower. As we can see in Figs. 8 and 9, the microspheres deform into hexagons and the structural color of photonic crystal films disappears when the heating temperature reaches 100 °C. Compared with the pure PMMA films, copolymer photonic crystal films are more heat-resistant.

The heat resistance of photonic crystal films can be identified by measuring the peak intensity at different temperatures. Fig. 10 shows the peak intensity of pure PMMA film and PMMA films with 10.3, 18.7, and 25.6 wt% MAA. For the pure PMMA film, the intensity decreases rapidly when the temperature increases to 90 °C (Fig. 10), and the intensity decreases to almost zero when the temperature is only 104 °C. The reflectance peak intensity of the PMMA photonic crystal films with 18.7 wt% MAA does not vary significantly before the temperature increases to 160 °C, which means that the close-packed structure is stable. Moreover, the intensity decreases dramatically to zero when the temperature is

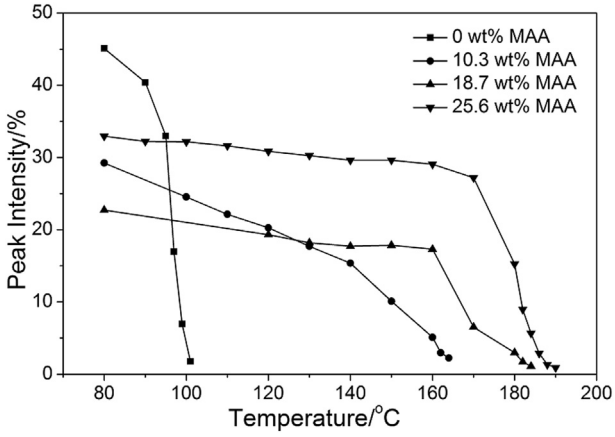

Fig. 10. Reflectance peak intensity of photonic crystal films with varying MAA contents at different temperature.

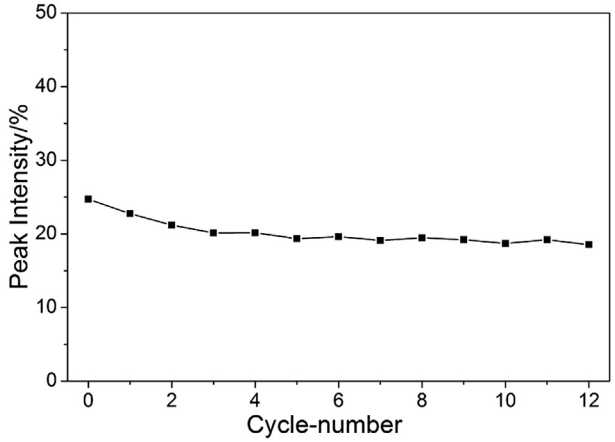

Fig. 11. Thermal cycling tests of PMMA photonic crystal films with 18.7 wt% MAA.

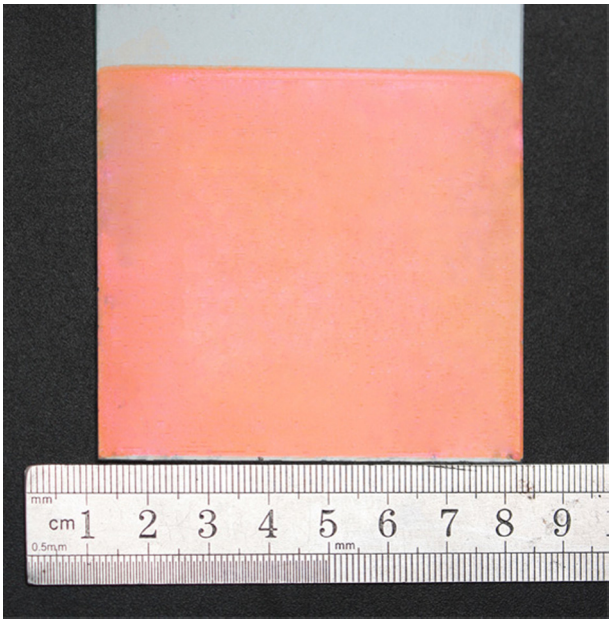

Fig. 12. Photograph of PMMA photonic crystal films with 18.7 wt% MAA manufactured in large-scale.

184 °C, which can be attributed to the damage in the spherical structure. This decrease is due primarily to the reduced magnitude of the optical dielectric contrast, which is proportional to reflection intensity [37]. Compared with the pure PMMA photonic crystal films, the heat resistance of the copolymer photonic crystal films that contain 18.7 wt% MAA improves dramatically.

The heat resistance of PMMA films was further proved by reversible temperature changes. Thermal cycling tests of PMMA photonic crystal films with 18.7 wt% MAA were carried out, and the results of a 12-cycle test were shown in Fig. 11. The samples are heated to 160 °C every time, and peak intensity changes only little after 12 cycles. The results also show that the films exhibit high heat resistance. In addition, the heat resistant PMMA film is manufactured in large-scale (Fig. 12), which meets requirements for practical applications, especially serving as painting materials.

4. Conclusions

In summary, the heat resistance of PMMA films that have a bright structural color is dramatically improved by using methacrylic acid as a comonomer. The mechanism of improving the heat resistance of PMMA was investigated. PMMA photonic crystal films with 18.7 wt% MAA could resist high temperatures up to 160 °C. And the peak intensity changes only little after thermal cycling tests, which indicates that the films have high heat resistance. In addition, not only are the materials cheap and the preparation process simple and feasible, but the obtained PMMA photonic crystal films also display brilliant visual color under natural lighting conditions. This study offers a new approach for generating highly heat-resistant and brilliant photonic crystal films, which will accelerate their application in daily life.

Acknowledgments

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